in the beginning itself and nitrate resulted in lower values. Out of all the anions tested, sulphate was found to be the most suitable anion in this procedure. Cu(II), Ni(II) and Fe(III) interfered in the determination. However, interference due to Cu(II) and Ni(II) up to 80 and 40 mg respectively could be minimized by masking with 15 g of ammonium tartrate. The results recorded in Table 2 show the comparison between homogeneous and conventional methods with regard to the separation from Cu(II) and Ni(II) using the masking agent. Five-fold excess of sodium and potassium did not interfere in the determination.

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Diamagnetic Susceptibilities of Compounds Containing C-Cl Bonds

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Magnetic susceptibilities of a number of compounds containing C-Cl bonds have been calculated using Pascal's, Gallais and Labarres', and Haberditzl's bond susceptibility data. While the values obtained using Pascal and, Gallais and Labbare's methods deviate to a great extent from the experimental values, values obtained using Haberditzl's method give good agreement.

French and Trew[1] have reported that experimental diamagnetic susceptibilities of halogen derivatives of methane differ very much from those calculated using Pascal's atomic susceptibility data. In this note diamagnetic susceptibilities (χ_M) for a number of compounds containing C-Cl bonds have been calculated using Pascal and Gallais and Labbares' methods[2]. The results are summarized in Table 1. Difference between calculated (by Pascal's or Gallais and Labbare's methods) and experimental χ_M values is more than 1% in all the cases and in some cases it is as high as 17%. In such calculations all factors except bond-bond interactions are duly accounted for. The anomalous results may thus be due to bond-bond interactions which do contribute to diamagnetism. χ_M values have been calculated using Haberditzl's bond susceptibility data also and the results are summarized in Table 1. In such calculations bond-bond interactions are duly accounted for. All the calculated values agree with the experimental values within 1%. Therefore, Haberditzl's wave-mechanical method can be applied to calculate molecular diamagnetism even for the compounds in which bond-bond interactions are significantly large. It can be inferred that bond-bond interactions are of large magnitude and contribute significantly to diamagnetism in compounds containing C-Cl bonds.

Table 1 — Diamagnetic Susceptibilities of Organic Compounds Containing C-Cl Bonds

Compound	Diamagnetic susceptibility $-\chi_M \times (10^{-6})$		
	Experimental*	Calculated using Pascal, Gallais and Labbare's data	Calculated using Haberditzl's data
Methyl chloride	32·00	33·95	32·15
n-Propyl chloride	56·10	56·75	56·05
Methylene dichloride	46·60	48·50	46·95
Chloroform	58·80	64·25	58·55
Carbon tetrachloride	66·80	80·00	66·95
Ethylidene chloride	57·42	61·10	57·10
1,1,2,2-Tetrachloroethane	87·48	91·40	86·90
Pentachloroethane	99·13	107·15	99·60
Hexachloroethane	112·80	122·90	112·20
Isoamyl chloride	78·92	80·75	79·45
2-Chloropropylene	47·80	48·95	48·05

*Literature values.

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Oxidation of Fluorenes by Ceric Ammonium Nitrate — A Kinetic Study

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Oxidation of fluorenes by ceric ammonium nitrate in acetic acid-nitric acid medium exhibits a first order dependence on each reactant. The reaction obeys the Hammett relationship, but the reaction constant ρ exhibits a direct dependence on the temperature. The magnitude of the isotope effect and the above temperature dependence of ρ indicate two different mechanistic pathways at 50° and 65°.

In the oxidation of cycloheptatriene[1], ceric ammonium nitrate (CAN) attacks selectively the π-bond rather than the hydrogen atoms of the active methylene group. We report another instance in the oxidation of fluorenes, wherein a similar selectivity by CAN, dependent on temperature is encountered.

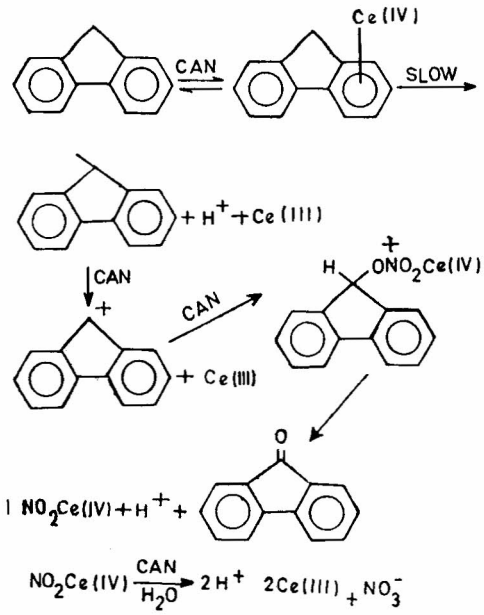
The kinetics of oxidation of fluorenes by CAN were followed in the presence of sodium acetate. Contrary to the usual Michaelis-Menten type of kinetics observed in the CAN oxidations of organic substrates this reaction curiously exhibits a clean first order dependence on the substrate (Table 1). The novel feature of this study is the finding that ρ, the reaction constant, has a direct dependence on temperature. The values of ρ at 50° and 65° are respectively −1·67 and −2·4. A plot of log $(k_2)_{65°}$ versus log $(k_2)_{50°}$ is linear with slope>1, indicating that selectivity increases with increase in temperature[2]. A kinetic isotope effect of 1·5 is observed for the oxidation of 9,9-dideuterofluorene at 50°. The data (at 50°) are consistent with a mechanism (Scheme 1) involving an attack at the 9-CH_2 function.

TABLE 1 — KINETIC DATA FOR THE OXIDATION OF FLUORENES BY CERIC AMMONIUM NITRATE IN THE PRESENCE OF SODIUM ACETATE

{[Ce(IV)] = 0·002*M*; [NaOAc] = 0·3*M*; [HNO_3] = 0·25*M*; solvent = HOAc-H_2O (80%-20%)}

[Substrate] *M*	Temp. °C	$k_1 \times 10^4$ (sec^{-1})	$k_2 \times 10^2$ (litre $mole^{-1}$ sec^{-1})
		FLUORENE	
0·012	50	1·23	1·03
0·015	50	1·96	1·30
0·020	50	2·23	1·12
0·025	50	3·41	1·30
0·030	50	3·48	1·16
0·012	57·5	—	3·72
0·012	65	—	8·33
		2-NITROFLUORENE	
0·012*	50	6·920	5·72
0·015*	50	8·30	5·53
0·0181*	50	10·13	5·61
0·012	50	—	0·07
0·012	57·5	—	0·11
0·012	65	—	0·14
		2-BROMOFLUORENE	
0·01194	50	0·68	0·57
0·01847	50	1·10	0·60
0·02403	50	1·44	0·60
0·012	57·5	—	0·96
0·012	65	—	1·53
		2-CHLOROFLUORENE	
0·0126	50	0·58	0·46
0·021	50	0·96	0·46
0·012	57·5	—	1·11
0·012	65	—	2·03
		2-IODOFLUORENE	
0·012	50	1·44	1·19
0·005965	50	—	1·17
0·012	57·5	—	3·46
0·012	65	—	4·77
		1-METHYLFLUORENE	
0·012	50	2·49	2·11
0·0202	50	4·34	2·15
0·012	57·5	—	4·87
0·012	65	—	16·25

*[Ce(IV)] = 0·002*M*; [NaOAc] = 0·3*M*; [HNO_3] = 0·35*M*; solvent = HOAc-H_2O (80-20%).



Scheme 1

Fluorenol is not an intermediate, since its reaction with CAN is slow, and no fluorenol has been isolated as the product.

In a series of similar reactions a linear correlation should be observed when logarithm of relative rate constants at two different temperatures are plotted against each other, with the slope equal to the ratio of the reaction constants and the intercept equal to zero. This conclusion follows from Hammett relationship thus:

$$\ln (k/k_H)_{T_1} = \rho_1\sigma$$
$$\ln (k/k_H)_{T_2} = \rho_2\sigma$$

Substituting for σ,

$$\ln (k/k_H)_{T_1} = \rho_1/\rho_2 \ln (k/k_H)_{T_2}$$

This is valid if the reaction follows Hammett relationship at both the temperatures. In fact very good individual linear relationships are observed with log *k* versus σ at 50° and at 65° ($\rho_{50°}$ = −1·66; corr. coeff.= 0·96; $\rho_{65°}$ = −2·4; corr. coeff.= 0·982). The above condition, however, is not fulfilled in a plot of log $(k/k_H)_{65°}$ versus log $(k/k_H)_{50°}$ in the oxidation of fluorenes by CAN indicating the operation of two different mechanisms. A similar plot in the V(V) oxidation of fluorenes gives excellent correlation (Fig. 1), showing that the same mechanism is operative at both the temperatures[4].

The magnitude of ρ at 65° in the oxidation of fluorenes by CAN indicates a more polar transition state. One way of explaining this large value is to consider Ce(IV) as a two electron oxidant (Scheme 2). This is quite unlikely. Also, the isotope effect, k_H/k_D = 1·06, clearly rules out the α-H abstraction in the rate determining step. A plausible explanation could be the formation of a cation-radical in the rate determining step, which is consistent with all the kinetic data and the selectivity of CAN to attack the π-bond (Scheme 3). Increase in temperature could facilitate a π→π* transition

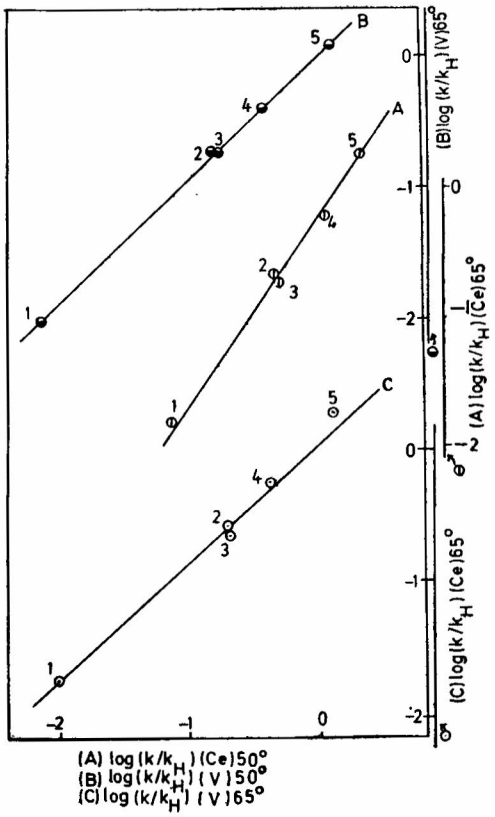
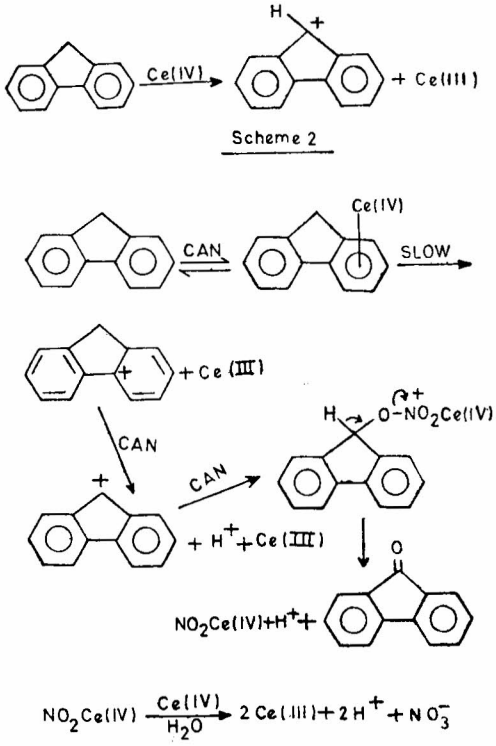


Fig. 1 — (A) log $(k/k_H)65°$ versus log $(k/k_H)50°$ in the case of oxidation of fluorenes by ceric ammonium nitrate. (B) log $(k/k_H)65°$ versus log $(k/k_H)50°$ in the case of oxidation of fluorenes by ammonium metavandate. (C) log $(k/k_H)65°$ for V(V) series versus log $(k/k_H)65°$ for Ce(IV) series. [(1) 2-Nitrofluorene, (2) 2-chlorofluorene, (3) 2-bromofluorene, (4) 2-iodofluorene and (5) 1-methylfluorene]



enabling CAN to abstract selectively an electron, resulting in the formation of a cation-radical.

Curiously, a plot of log $|(k/k_H)_{CeIV}$ versus $\log(k/k_H)_{V(V)}$ at 65° gives a very good correlation, indicating similar transition state in both the oxidation series.

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Effect of Structure on Activation Parameters

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The effect of substituents on the activation parameters has been discussed. The trend observed is explained on the basis of energies of the ground state and activated complex.

In the oxidation of fluorenes by ammonium metavanadate, a good linear free energy relationship as evidenced by a satisfactory Hammett plot was obtained[1]. But a plot of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (the isokinetic plot) showed a marked deviation for the 2-nitrofluorene molecule. In view of a recent communication[2] on the nature of variations of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ with σ, we have analysed our results in a similar fashion and the results are reported in this note.

The rate constants for the V(V) oxidation of the 2-substituted fluorenes and the derived activation parameters are presented in Tables 1 and 2.

The enthalpy of activation of the reaction increases with decrease in the electron density at the reaction centre as revealed by σ values of the 2-substituents. These data do not have a linear

Table 1 — Temperature Dependence of the Rate Constants

[[V(V)] = 0·004*M*; [substrate] = 0·024*M*; μ = 3·5; [H_2SO_4] = 1·0*M*; solvent: 80% HOAc-20% H_2O (v/v)]

Substrate	$k_2 \times 10^2$ (litre mole^{-1} sec^{-1}) at		
	50°	57·5°	65°
1-Methylfluorene	2·98	4·98	9·97
Fluorene	2·38	4·26	8·02
2-Iodofluorene	0·88	1·57	3·21
2-Chlorofluorene	0·33	0·74	1·56
2-Bromofluorene	0·39	0·75	1·65
2-Nitrofluorene	0·017	0·038	0·077
2-Ethylfluorene	74·12	46·00*	27·23†

*At 40°. †At 30°.